CHARGE CARRIER GENERATION AND EXCITON QUENCHING AT M3EH-PPV/SMALL-MOLECULE AND M3EH-PPV/OXIDE INTERFACES

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ABSTRACT

The need for efficient exciton dissociation is one of the most important factors limiting improved efficiencies in organic photovoltaic devices. Using luminescence as a probe, we studied the quenching of excitons in semiconducting polymers for a variety of quenching materials, including transparent conducting oxides (TCOs) and small molecule perylene diimide thin films. Perylene benzimidazole (PBI) is shown to be the best quencher of those studied. This result is consistent with the improved conversion efficiencies demonstrated when this material is used in a polymer bilayer photovoltaic device.

INTRODUCTION

Polymer-based solar cells offer the potential for large-area, low-cost solar energy conversion using environmentally friendly materials. To accomplish this, carriers must be effectively generated and collected. Unlike inorganic solar cells, electrons and holes are not immediately formed upon light absorption in organic photoactive materials. Instead, bound electron-hole pairs (excitons) are created. The exciton binding energy must be overcome in order to dissociate the excitons to free charges. Charge carrier collection results in the subsequent generation of current from the device. Any charges that are not dissociated within the exciton lifetime will recombine by non-radiative or radiative decay. For many materials, the electric fields present in organic devices are not strong enough to directly dissociate excitons, and, therefore, most exciton dissociation occurs via a charge transfer process at the interfaces between materials of high electron affinity and low ionization potential [1, 2]. Such exciton dissociation results in a decrease in the luminescence intensity. Our current work uses photoluminescence (PL) to investigate exciton generation and quenching (dissociation) in semiconducting conjugated polymers for a variety of quenching materials, including various transparent conducting oxides (TCOs) and organic small molecule thin films.

EXPERIMENT

Materials

For the purpose of this study, we selected an optically-active, semiconducting conjugated polymer: poly[2,5-dimethoxy-1,4-phenylene-1,2-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-1,2-ethenylene (M3EH-PPV). This polymer is a hole transporter, absorbing in the range of 400-600 nm with a relatively high absorption coefficient of 2.3×10^5 cm^{-1} at 500 nm [3].

We utilized various TCOs and small molecule thin films as possible quenching interfaces. The TCOs surveyed include indium tin oxide (ITO), tin oxide (SnO_2) and titanium oxide (TiO_2). We also considered the following perylene diimides in thin film: perylene benzimidazole (PBI), perylene bis(piridylethylimide) (PPyEI) and perylene-bis(phenethylimide) (PPEI). All perylene compounds underwent purification by thermal gradient sublimation. Chemical structures for these organic materials are shown (see Fig. 1).
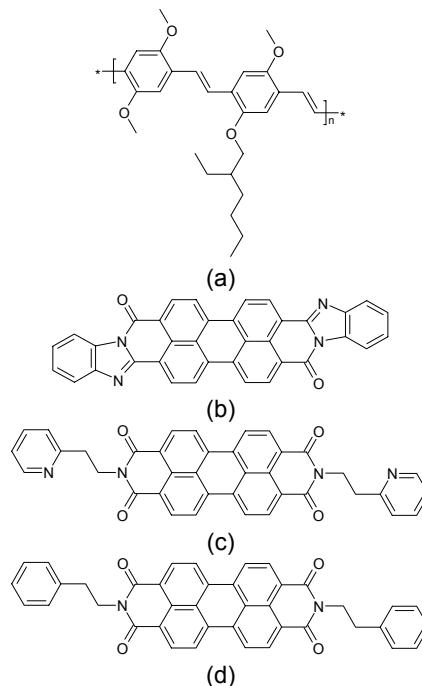

Fig. 1.   Chemical structures for (a) M3EH-PPV, (b) PBI, (c) PPyEI and (d) PPEI.

Sample Preparation

Substrates for the study included plain glass laboratory slides and glass slides with deposited oxide layers. The slides used in the quenching studies were

cleaned with ethyl alcohol, submerged in a potassium hydroxide basic bath for 20 minutes, rinsed in deionized water, and finally dried with nitrogen gas.

M3EH-PPV was dissolved in a 0.4 g/mL chlorobenzene solution and spin cast to form thin films of 10-15 nm thickness on both the plain glass and the oxide-coated slides for the perylene and oxide quenching experiments, respectively. In order to achieve smoother films, the polymer films were heated to 75 °C under rough vacuum (30 torr) for one hour. As previously demonstrated, this annealing method improves the charge transport properties of the polymer [4]. For the small molecule quenching experiments, each perylene material was thermally evaporated ($\sim 10^{-6}$ torr) to a thickness of approximately 30 nm, measured via a quartz crystal monitor, on top of a partially masked polymer layer. The unexposed polymer film served as a reference during PL measurements. A separate sample of polymer on quartz provided the reference for the oxide samples.

Photovoltaic devices using polymer/perylene bilayers are constructed in a manner similar to that described above. Commercial slides of patterned ITO on glass were cleaned first in an isopropanol ultrasound bath and then in oxygen plasma at 150 W for five minutes. Polymer films of roughly 40 nm were fabricated using a 0.8 g/mL solution of M3EH-PPV in chlorobenzene while perylene layers are evaporated to about 10-20 nm. In addition to the polymer/perylene deposition order used for the luminescence quenching studies, we also constructed reversed devices by evaporating the perylene directly onto the ITO and then spin casting the polymer layer. Approximately 50 nm of gold was thermally evaporated to form the top electrode.
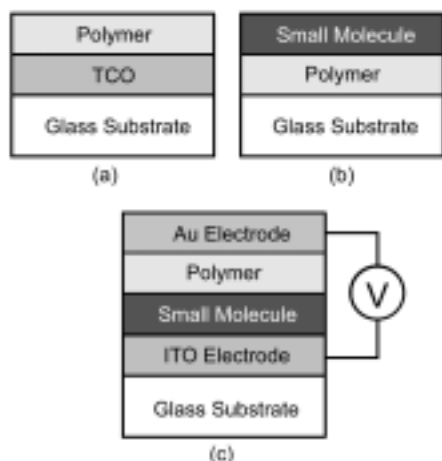

Fig. 2.   Device structures for the luminescence quenching experiments with (a) oxides and (b) perylene diimides; device structure for photovoltaic cells (c) .

Characterization Methods

To prevent photo-oxidation of the polymer, all devices were stored and measured under an inert nitrogen or argon atmosphere.

Photoluminescence (emission) spectra were measured in a 180-degree backscattering configuration with an Ar-ion laser operating at 488 nm and a single grating Spex 270M spectrometer with an LN_2 cooled CCD array detector. A holographic notch filter was used to suppress the laser line at the spectrometer entrance slit. The incident laser power was typically 0.2 – 50 μW. All samples were oriented such that the incident beam encounters the polymer layer first.

Due to high dispersion of the 1200 gr/mm grating, six overlapping spectra with central wavelengths ranging from 500 to 800 nm were measured in order to capture the entire photoluminescence spectra of the polymer. Using translation stages, the sample was repositioned without changing the focal point. This method allows for comparative spectra to be obtained for both the quenched and unquenched regions.

For photovoltaic devices, J-V curves were taken both in the dark and light using a source-measure unit (Keithley 236). A xenon lamp provided white light illumination of 100 mW/cm^2, calibrated by a power meter.

RESULTS AND DISCUSSION

Luminescence Quenching

Exciton quenching of the M3EH-PPV is observed with all materials studied (see Table 1). By comparing the relative fluorescence of each sample in the unquenched and quenched regions, it is determined that PBI and PPEI are the most efficient quenching materials of those studied, decreasing the observed PL by approximately 90%. Figure 3 illustrates representative spectra for PPEI, PPvEI and TiO$_2$. It should be noted that interference effects resulting from the difference in refractive indices at the interface is not compensated for in this data [4].

Quenching Material	$1- \dfrac{\text{Unquenched PL}}{\text{Quenched PL}}$
PPEI	0.9018
PBI	0.9008
PPyEI	0.7274
SnO$_2$	0.6652
ITO	0.5478
TiO$_2$	0.5407

Table 1.   Relative Quenching Efficiencies of Surveyed Materials at Peak Fluorescence of M3EH-PPV.

With respect to the M3EH-PPV/TCO interface, the primary quenching mechanism is electron transfer as described by:
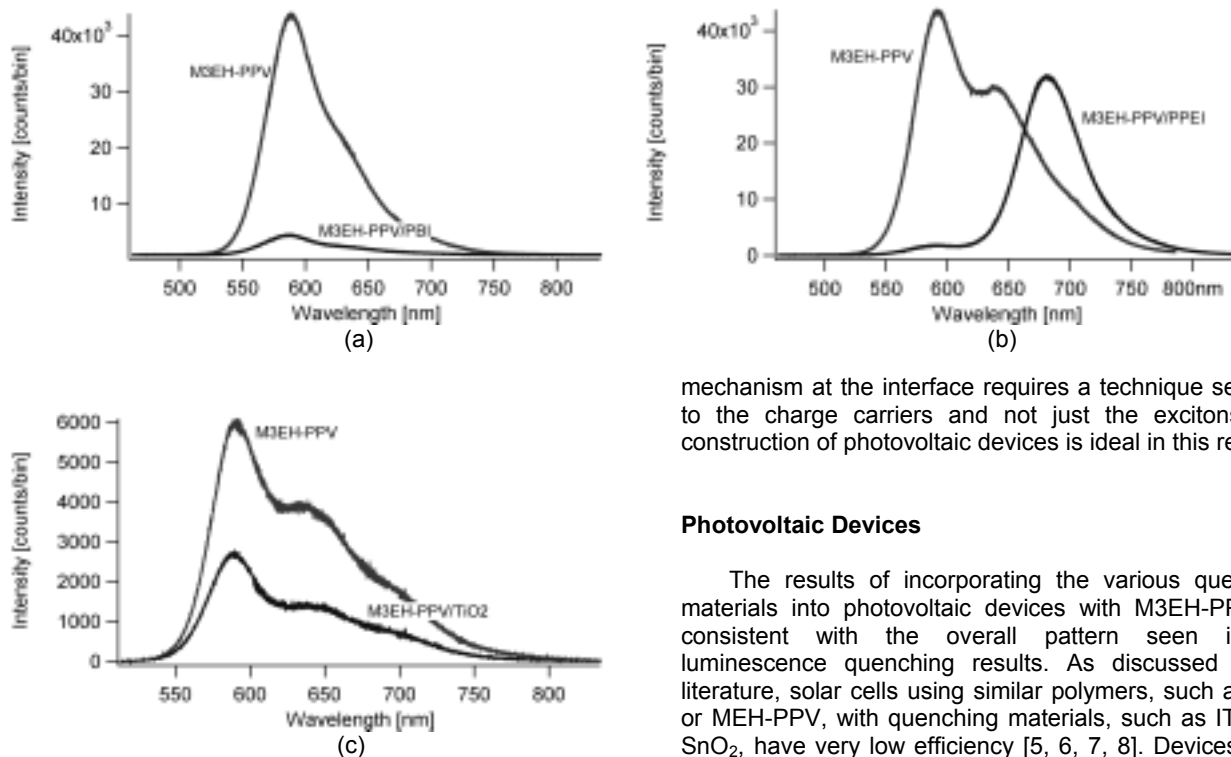
$$D^* + A \longrightarrow D^+ + A^- \qquad (1)$$

(a)

(b)

(c)
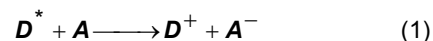
Fig. 3.   Comparison of PL spectra for M3EH-PPV (a) unquenched , PBI-quenched (b) unquenched, PPEI-quenched   (c) unquenched, TiO₂-quenched. The PPyEI sample followed the same trend as the PBI-related spectra with a lesser degree of quenching. The TiO2-related spectra are representative of those for all TCOs studied.

where D represents the donor (polymer) and A is the acceptor (TCO). For the materials studied, the relative quenching efficiencies did not differ significantly. (see Fig. 3)

At the M3EH-PPV/perylene interface, a combination of electron transfer and exciton transfer may be occurring. The exciton transfer is described by:

$$D^* + A \longrightarrow D + A^* \qquad (2)$$
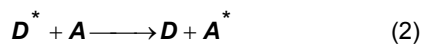
where A* can decay radiatively or non-radiatively. Both PBI and PPEI act as comparable quenching materials of the polymer fluorescence, reducing the emission by 90% of its initial, unquenched value.

For the PPEI/M3EH-PPV films, there is clear evidence of emission from the PPEI, which peaks at 690 nm. The intensity of the emission exceeds that of a PPEI film alone, demonstrating efficient energy transfer from the M3EH-PPV to the PPEI. Although pure films of PBI and PPvEI emit when excited directly at 488 nm, there is no evidence of emission from these perylenes when deposited onto the M3EH-PPV film, which continues to emit at a quenched intensity. This data suggests that a different quenching mechanism is occurring: electron transfer. To verify the existence of this exciton dissociation

mechanism at the interface requires a technique sensitive to the charge carriers and not just the excitons. The construction of photovoltaic devices is ideal in this respect.

Photovoltaic Devices

The results of incorporating the various quenching materials into photovoltaic devices with M3EH-PPV are consistent with the overall pattern seen in the luminescence quenching results. As discussed in the literature, solar cells using similar polymers, such as PPV or MEH-PPV, with quenching materials, such as ITO and SnO₂, have very low efficiency [5, 6, 7, 8]. Devices using TiO₂, on the other hand, exhibit almost an order of magnitude higher efficiency [7, 8]. While not directly related to quenching efficiency, this difference in device performance is thought to be due to issues regarding the direction of charge flow and a large disparity between the values of the electron and hole mobilities [9, 10]. Devices of the type ITO/TiO₂/M3EH-PPV/Au have shown conversion efficiencies up to η = 0.46% under 100 mW/cm^2 white light illumination [11].

However, the photovoltaic devices in this study of the type ITO/PBI/M3EH-PPV/Au demonstrate promising improvements in efficiency compared to devices made from either photoactive material alone and to other planar (non-blended) heterojunction organic devices. Conversion efficiencies of η = 1.6% are achieved for 100mW/cm^2 white light. We attribute this increase, compared to the TiO₂ devices, to both the higher exciton quenching efficiency as seen in the luminescence studies and the contributions of both heterojunction materials to the photocurrent. Photoaction current spectra (data not shown) show that both organic materials contribute to the photocurrent: excitons produced in each material diffuse to the PBI/M3EH-PPV interface where they are dissociated, with electrons transferred to the PBI and holes to the M3EH-PPV. Overall, these results confirm that charge transfer, rather than energy transfer, is primarily responsible for the exciton quenching at the PBI/M3EH-PPV interface seen in the luminescence experiments. Reversing the order of the photoactive layers to create an ITO/M3EH-PPV/PBI/Au device reverses the direction of the photocurrent and photovoltage, consistent with the direction of exciton dissociation described above. Devices
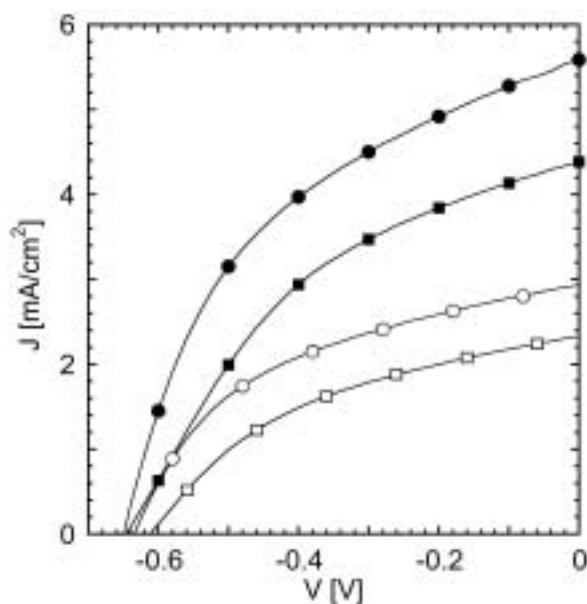
Fig. 4. J-V curves for devices ITO/PBI/M3EH-PPV/Au (circles) and ITO/PPyEI/M3EH-PPV/Au (squares) for white light intensities of 100 mW/cm^2 (filled symbols) and 50 mW/cm^2 (open symbols).

made with PPyEI in place of PBI show similar results, though with slightly lower photocurrents (Fig. 4).

CONCLUSIONS

We investigated improving the efficiency organic bilayer photovoltaic devices using semi-conducting polymers with a variety of exciton quenching materials. Exciton dissociation only occurs at interfaces between materials. Combined with the short exciton diffusion lengths (generally 10-20 nm) in organic materials, this limitation makes exciton dissociation one of the most important factors limiting conversion efficiencies in solid-state organic solar cells. We have explored a variety of possible quenching materials, both transparent conducting oxides and organic small molecule films, in order to maximize the exciton quenching efficiency. Luminescence quenching experiments have demonstrated that the oxides quench excitons relatively well while small molecule perylene diimides tend to be the best quenchers. Due to their photoactive properties, these small molecule thin films enhance the performance of the photovoltaic devices in that this allows for an increase in the absorption range and the effective charge generation region in the bilayer solar cell. We have achieved conversion efficiencies up to 1.6% under one-sun intensities for perylene/polymer bilayer devices. While low compared to dye-sensitized and inorganic solar cells, this result is an improvement compared to other polymer-based non-blended photovoltaic devices.

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